Spin–state polaron in lightly hole-doped $LaCoO_3$

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Abstract

Inelastic neutron scattering (INS), electron spin (ESR) and nuclear magnetic resonance (NMR) measurements were employed to establish the origin of the strong magnetic signal in lightly hole-doped $La_{1-x}Sr_xCoO_3$, $x \sim 0.002$. Both, INS and ESR low temperature spectra show intense excitations with large effective g-factors $\sim 10 - 18$. NMR data indicate the creation of extended magnetic clusters. From the Q-dependence of the INS magnetic intensity we conclude that the observed anomalies are caused by the formation of octahedrally shaped spin-state polarons comprising seven Co ions.

Physical properties of nanostructured magnetic materials are extensively studied because of their fundamental interest and potential applications. A naturally occurring analog to the artificially fabricated heterostructures are doped perovskites with intrinsic inhomogeneities (magnetic phase separation), i.e. with a spatial coexistence of magnetic clusters in a nonmagnetic matrix. Hole-doped cobaltites $La_{1-x}Sr_xCoO_3$ with perovskite-type structure exhibit ferromagnetic (FM) clusters [1, 2, 3] causing spin-glass and superparamagnetic behavior for $0.05 \lesssim x \lesssim 0.2$ below and above a critical magnetic blocking temperature T_g, respectively [4]. Due to a progressive change with increasing temperature from low- (LS) to intermediate- (IS) or high-spin (HS) states of the cobalt ions a reentrant metal-insulator (MI) transition was found for $0.2 \lesssim x \lesssim 0.3$ within $100 \lesssim T \lesssim 200$ K [4]. With the addition of charge carriers the number and possibly size of clusters grow leading to a percolation-type long-range FM order and MI transition at $x \gtrsim 0.2$ [3, 4, 5].

Most of the investigations up to now have been focused on relatively high Sr concentration ($x > 0.1$). It is widely believed that the addition of each hole into pristine $LaCoO_3$ through the substitution of a divalent ion for La^{3+} creates a Co^{4+} ion in the lattice which has a nonzero S in any spin state configuration, thereby inducing a magnetic moment in the system. An amazing fact was found by Yamaguchi et al. in 1996 [6] and apparently forgotten later. Namely, already lightly doped material with $x \sim 0.002$ (i.e. with an estimated concentration of only two holes per thousand Co^{3+} ions) exhibits unusual paramagnetic properties at low temperatures: few embedded spins in a nonmagnetic matrix give an order of magnitude larger magnetic susceptibility than expected. It was proposed that a doped hole in the spin-singlet ground state of $LaCoO_3$ behaves as a localized magnetic impurity with unusually large spin value $S = 10 - 16$ [6] due to the formation of a magnetic polaron whose nature, however, remained unclear. Later, and for higher Sr-doping $x > 0.05$, it was surmised that the addition of charge carriers forms Zener-type polarons or even many-site magnetopolarons [2, 3]. However, experimental proof of the existence of such polarons is missing so far.

In this Letter, we elucidate the mechanism of how already the light hole doping $x \sim 0.002$ dramatically affects magnetic properties of $LaCoO_3$. Combining INS data, obtained with and without external magnetic field, with the single crystal ESR and NMR measurements on $La_{0.998}Sr_{0.002}CoO_3$, we find that the charges introduced by substitution of Sr^{2+} for La^{3+} do not remain localized at the Co^{4+} sites. Instead, each hole is extended over the neighboring

Co^{3+} ions, transforming them to higher spin state and thereby forming a magnetic seven-site (heptamer) polaron.

Highly stoichiometric powder and single crystal samples of $La_{1-x}Sr_xCoO_3$, $x = 0$, 0.002 were synthesized and characterized according to procedures described elsewhere [7]. The INS measurements were performed on the high-resolution time-of-flight spectrometers NEAT (Hahn-Meitner-Institut, Berlin, Germany) and FOCUS (Paul Scherrer Institut, Villigen, Switzerland). The data were collected using incoming neutron energies $3.26 - 3.5\,\mathrm{meV}$, giving an energy resolution at the elastic position of $\sim 0.09 - 0.15\,\mathrm{meV}$. Raw data were corrected for sample self-shielding and detector efficiency according to standard procedures. The DAVE software package was used for elements of the data reduction and analysis [8]. High field ESR measurements were performed with a home-made spectrometer based on a Millimeterwave Vector Network Analyzer (MVNA) from AB Millimetrè at frequencies 27 - 550 GHz for the magnetic field B parallel to the [001] pseudo-cubic axis of the single crystal (see technical details in Ref. 9). In the same field geometry ^{59}Co ($I = 7/2$) NMR was measured at a frequency of 47.65 MHz with a Tecmag pulse NMR spectrometer.

The susceptibility data (not shown) are similar to those of Ref. [6]. In order to estimate an effective magnetic moment of doped holes we fitted measured magnetization $M(H)$ with a combination of the conventional Brillouin function $B_S(y)$ and a field-linear term, $M(H) = N\mu_B gS \cdot B_S(y) + \chi_0 H$, $y = (g\mu_B SH)/(k_B T)$. Assuming a hole concentration $N = 0.002$, we found $gS \sim 15\mu_B$/hole, which is much larger than we can expect from Co^{3+} or Co^{4+} in any spin-state, and which agrees with [6].

Zero-field inelastic neutron spectra of $La_{0.998}Sr_{0.002}CoO_3$ are shown in Fig. 1 a. In contrast to the parent compound $LaCoO_3$, where no excitations have been found for $T < 30\,\mathrm{K}$ [10], an inelastic peak at 0.75 meV was observed down to $T = 1.5\,\mathrm{K}$. One more inelastic peak at 0.6 meV was found at intermediate temperatures starting from $T \sim 30\,\mathrm{K}$ similar to that found in pristine $LaCoO_3$ [10]. Clearly the peak at 0.6 meV corresponds to the signal from the undisturbed matrix. We can thus interpret the peak observed at 0.75 meV as a signal which is due to Sr doping [7]. Already a weak magnetic field splits the transition into two lines whose widths widen considerably with increasing field strength (Fig. 1 b). The Zeeman splitting is enormous and can be explained with a g-factor of the order of 10 in agreement with the aforementioned macroscopic measurements.

Similarly to INS, the undoped $LaCoO_3$ exhibits no bulk ESR signal for $T \leq 30\,\mathrm{K}$ [11].

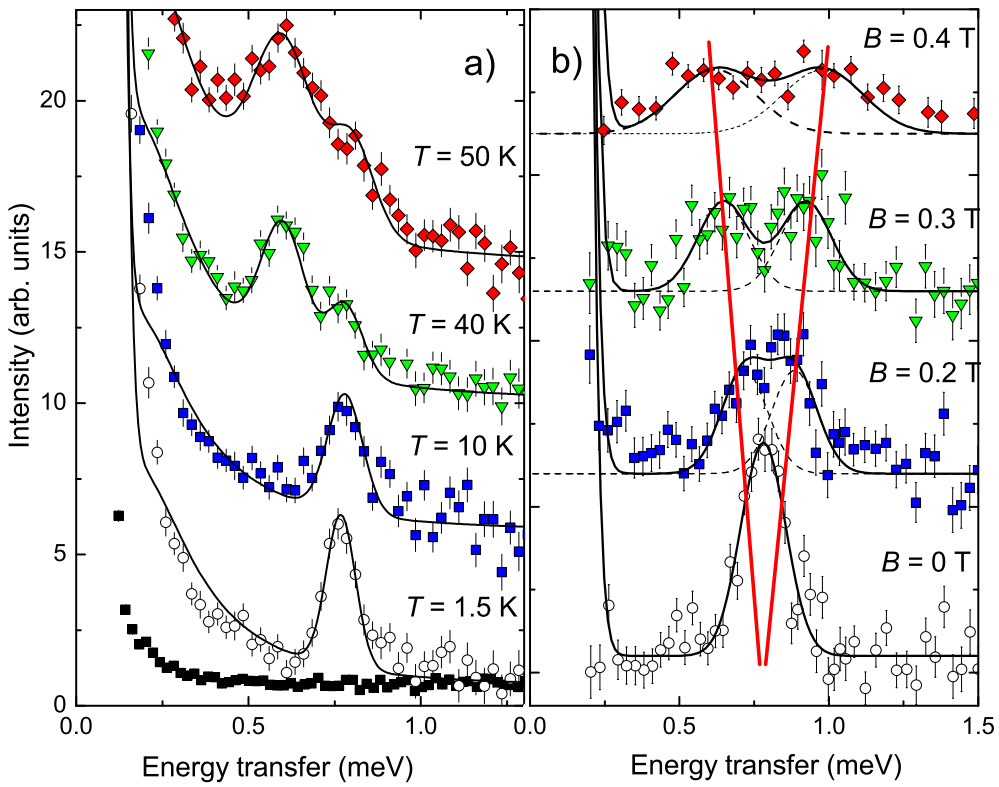

FIG. 1: (Color online) Temperature ($B = 0$) and magnetic field ($T = 1.5\,\mathrm{K}$) evolutions of the INS spectra of $La_{0.998}Sr_{0.002}CoO_3$ measured on FOCUS and NEAT, respectively. Solid black squares correspond to data taken from nonmagnetic $LaAlO_3$ at $T = 50\,\mathrm{K}$, black lines refer to least-squares fits of Gaussian functions, red lines are guides to the eye.

However, in $La_{0.998}Sr_{0.002}CoO_3$ we observe a very intense ESR spectrum consisting of 7 absorption lines (Fig. 2 a,b). The dependence of their resonance fields B^i_{res} on the frequency ν (resonance branches) reveals that most of the excitations are gapped with a gap value $f_0 \approx 170\,\mathrm{GHz} \approx 0.7\,\mathrm{meV}$ (Fig. 2 a,b), in nice agreement with the energy of the low-T INS peak. The effective g-factors of the most intense branches $g_i = (h/\mu_B)(\partial\nu/\partial B)_i$ are significantly larger than a spin-only value of 2 and vary from $\sim$ 2.1 to $\sim$ 18.3. With increasing T the intensity of these lines strongly decreases whereas above $\sim 35\,\mathrm{K}$ two new lines (marked A and B in Fig. 2 a,b) emerge. Their branches (not shown) yield a gap $f_1 \approx 150\,\mathrm{GHz} \approx 0.6\,\mathrm{meV}$ and a g-factor ≈ 3.43. The behavior of A and B is very similar to the ESR data in Ref. 11 for *undoped* $LaCoO_3$ which allows to unambiguously identify these lines with the thermally activated Co^{3+} HS state ions and thus with the thermally activated

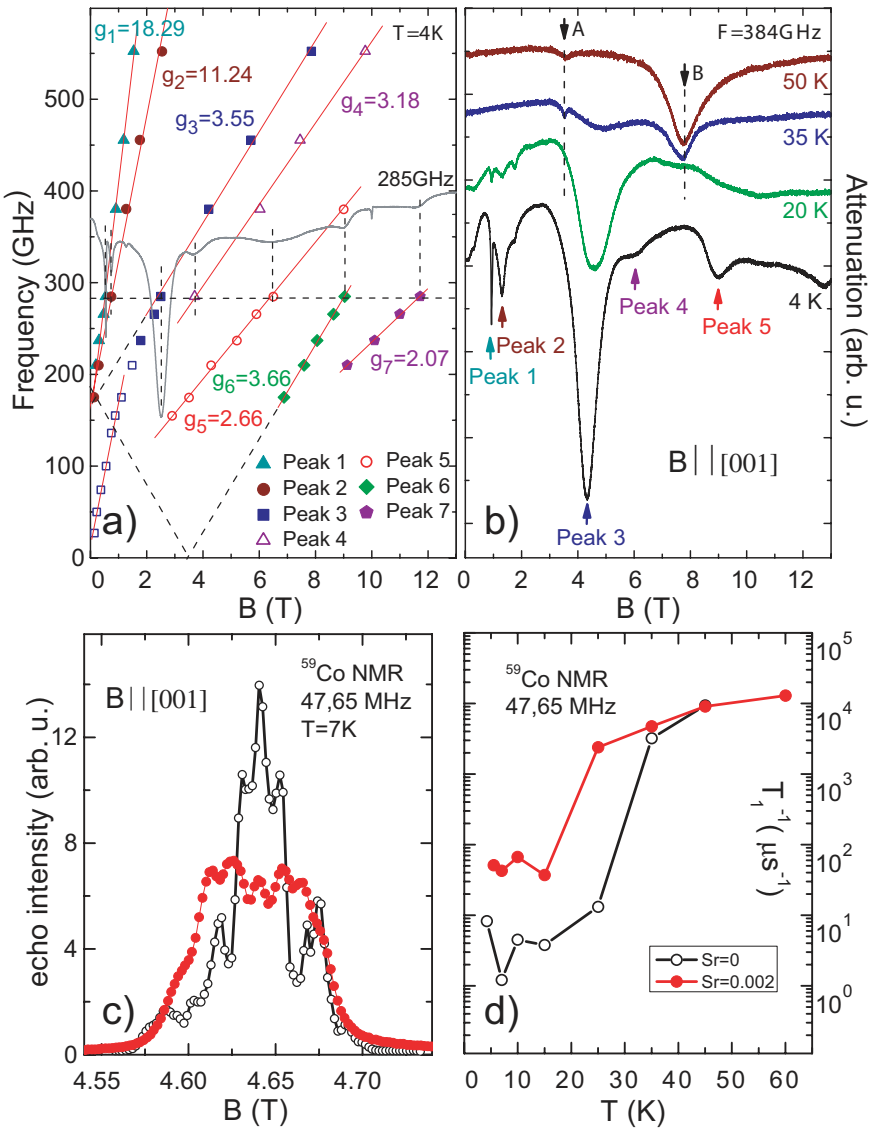

FIG. 2: (Color online) a) Frequency vs. magnetic field dependence (branches) of the ESR modes of the low-T spectrum. Straight lines through data points are linear fits (see text). Open squares denote a small presumably impurity peak visible below ~ 200 GHz. b) T-dependence of the ESR spectrum at 384 GHz. A and B label ESR modes due to thermally activated Co^{3+} HS state ions. c) and d) Low-T ^{59}Co NMR spectra and T-dependences of the nuclear relaxation rate T_1^{-1}, respectively, for $LaCoO_3$ and $La_{0.998}Sr_{0.002}CoO_3$ single crystals (open and closed circles). Lines connecting the data points are guides for the eye.

INS peak [10].

The strong low-T ESR response of $La_{0.998}Sr_{0.002}CoO_3$ cannot be explained by the occur-

rence of isolated Co^{4+} ions with an effective spin $\tilde{S} = 1/2$ in the LS state or isolated Co^{3+} in the HS or IS state with $\tilde{S} = 1$. A large number of lines implies the existence of resonating centers with larger spin multiplicity, since, e.g., for $\tilde{S} = 1$ not more than 3 lines can be expected. Therefore the ESR data strongly suggest that small Sr (i.e. hole) doping results in the formation of spin clusters with large effective g-factors involving several interacting magnetic Co sites.

The ^{59}Co NMR data are summarized in Fig. 2 c,d. The spectral shape and the spin-lattice relaxation rates of the undoped $LaCoO_3$ agree very well with previous ^{59}Co-NMR studies [12, 13]. According to a simple estimate, doping with 0.2 % Sr, that yields 0.2 % of Co^{4+} sites, should change the electric field gradient for at most 5 % of nuclei. It means that the doping induced change of the low-T spectrum, that gets barely resolved (Fig. 2 c), is not due to the quadrupole interaction and has probably magnetic origin. It becomes even more apparent in the nuclear spin dynamics yielding at low T a more than 15 times enhanced relaxation rate T_1^{-1} (Fig. 2 d). The observed stretch-exponential shape of the nuclear magnetization recovery suggests a substantially non-uniform distribution of local magnetic environments at low T seen by the Co nuclei [14]. Thus ^{59}Co-NMR data of $La_{0.998}Sr_{0.002}CoO_3$ clearly indicate the formation of spatially extended magnetic clusters at low T. In contrast, above ~ 35 K, where a considerable part of Co ions is in the thermally activated HS state, the NMR spectra and relaxation for doped and undoped samples are very similar, and the shape of the nuclear magnetization recovery testifies an almost homogeneous distribution of magnetic centers [15].

Thus, a contribution of several Co-ions, i.e. the formation of magnetic clusters is required to explain the results of our magnetic susceptibility, INS, ESR and NMR measurements. The hole is not localized on one particular ion but dynamically distributed over the cluster. A reasonable mechanism for such a resonant state was proposed by Louca and Sarrao [2]. Neighboring LS-Co^{4+} and IS-Co^{3+} ions can share an e_g electron by swapping configuration. The t_{2g} electrons, in turn, couple ferromagnetically via double exchange interaction. Therefore, we propose that the holes introduced in the LS state of $LaCoO_3$ are extended over the neighboring Co sites forming spin-state polarons and transforming all involved Co^{3+} ions to the IS state. An important question remains: How many Co ions are involved in a single hole-doped cluster?

The wave-vector dependence of the intensity of the INS signal yields direct information

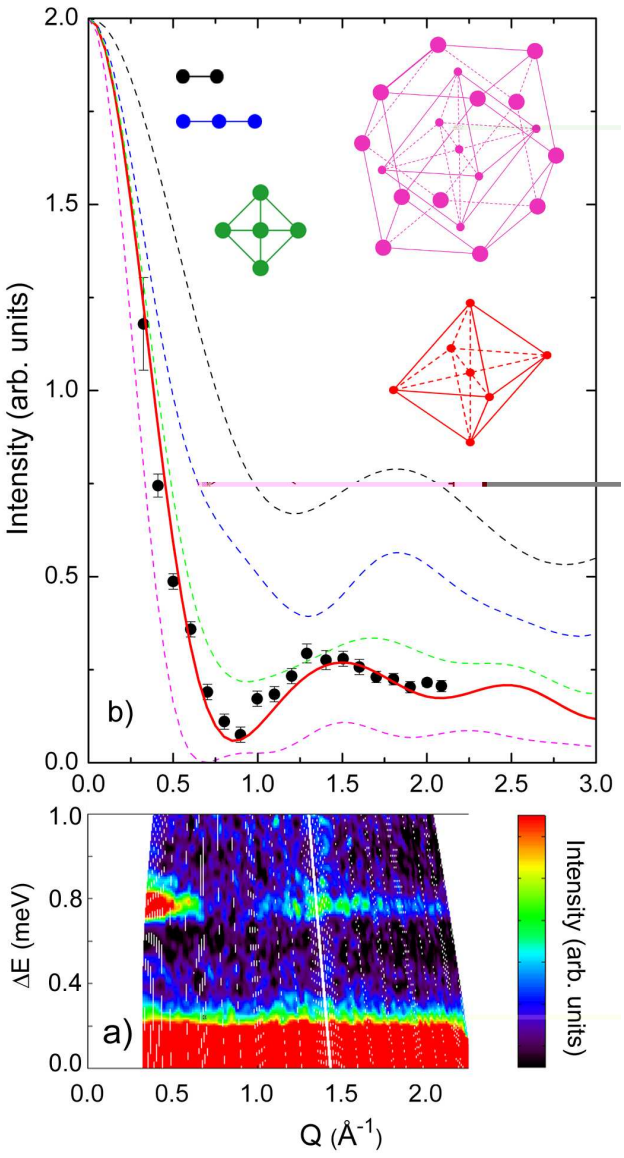

FIG. 3: (Color) a) Excitation INS spectrum collected on FOCUS from $La_{0.998}Sr_{0.002}CoO_3$ at $T = 1.5\,K$. b) Circles: Experimental Q dependence of the intensity of the peak observed at 0.75 meV. Lines: Calculated Q dependence of the neutron cross section [Eq. 1] for different Co multimers (visualized in the figure) in the cubic perovskite lattice of $LaCoO_3$ and for $|S\rangle \Rightarrow |S\rangle$ transitions. The nearest neighbor Co–Co distance was fixed at $R_{Co\text{-}Co} = 3.9\,Å$ determined for $La_{1-x}Sr_xCoO_3$ from the Co-O pair density function [2].

about the geometrical configuration of the magnetic ions in the cluster. We studied in detail the Q dependence of the 0.75 meV peak for $0.4 \leqslant Q \leqslant 2.0\,Å$. The excitation is dispersionless

indicating that intercluster interactions can be neglected (Fig. 3 a). The intensity of the observed transition exhibits a clear oscillatory behavior reflecting the size as well as the shape of a spin-state polaron through the structure factor. For a cluster comprising n magnetic ions, the neutron cross section for polycrystalline materials is given by [16]:

$$\frac{d^2\sigma}{d\Omega d\omega} \quad \propto \quad F^2(Q) \sum_{j<j'=1}^{n} \left(|\langle S\|T_j\|S'\rangle|^2 + 2\frac{\sin(Q|R_j - R_{j'}|)}{Q|R_j - R_{j'}|}\langle S\|T_j\|S'\rangle\langle S'\|T_{j'}\|S\rangle \right), \quad (1)$$

where $F(Q)$ is the magnetic form factor, Q the scattering vector, R_j the position vector of the j-th ion in the cluster, and T_j an irreducible tensor operator of rank 1 [17]. This cross section corresponds to a superposition of damped sine functions which reflect the geometry of the cluster. Each particular transition $|S\rangle \Rightarrow |S'\rangle$ has its specific Q dependence due to both the sign and the size of the reduced matrix elements. Lines in Fig. 3 b correspond to calculated cross sections for different Co clusters in the cubic approximation of the perovskite lattice of $LaCoO_3$ and for the special case of a $|S\rangle \Rightarrow |S\rangle$ transition [18], which, as will be seen below, is relevant in the context of the present work. We clearly see that the Q dependence of the cross section is an unambiguous fingerprint of the geometry of the multimers; in particular, the data observed for the 0.75 meV transition in $La_{0.998}Sr_{0.002}CoO_3$ are perfectly explained by the scattering from *an octahedrally shaped Co heptamer* (see Fig. 3 b, red heptamer and red solid line). Total moment of this heptamer (consisting formally of one LS Co^{4+} ($S = 1/2$) and six IS Co^{3+} ($S = 1$) is 15 μ_B, in exact agreement with our magnetic measurements.

Considering only nearest-neighbor coupling J between a central Co^{4+} ion in the LS state and six Co^{3+} ions in the IS state, the Heisenberg exchange Hamiltonian is given by $H_{ex} = -2J\vec{S}_1 \cdot \vec{S}_A$, where $\vec{S}_A = \vec{S}_2 + \ldots + \vec{S}_7$ and the total spin is $\vec{S} = \vec{S}_1 + \vec{S}_A$. The Co-Co coupling J is ferromagnetic via the double exchange mechanism [2]. The ground state of the cobalt heptamer is therefore the state with maximum spin quantum numbers, namely $|\ S_1, S_A, S\rangle = |\ 1/2, 6, 13/2\rangle$. The first excited state $|\ 1/2, 5, 11/2\rangle$ lies higher up by J. The exchange coupling J of cobalt oxides is of the order of 10 meV [19], thus, the first excited multiplet heptamer state lies far above the energy window covered by the present experiments. What is then the origin of the peak observed at 0.75 meV? As argued above, even light doping promotes neighboring Co^{3+} to an IS state already at T=0. The ground state of the Co^{3+} ions in the IS state comprising the main part of the magnetic polarons is an orbitally degenerate triplet (see Ref. 10, Fig. 4 (right)) which is split by a small trigonal field into a singlet and doublet. Transition between these levels is, in our opinion, the source

of the 0.75 meV peak. In fact, the temperature dependence of the intensity supports the singlet-doublet nature of the peak at 0.75 meV, see Fig. 1 a. Here, this transition due to a magnetic (IS) Co^{3+} exists already at $T = 0$, whereas for the undoped system the similar transition at 0.6 meV is only due to thermally-activated magnetic (HS) state [10]. The complete ground-state wave function of the Co^{3+} heptamer has to be written as a combined spin-orbit product state of the form $\mid S_1, S_A, S\rangle \mid L, M_L\rangle$, thus the intensities of both spin and orbital excitations are governed by the structure factor of the cobalt heptamer described by Eq. 1.

To summarize, we have investigated lightly doped cobaltite $La_{0.998}Sr_{0.002}CoO_3$ by means of INS, ESR and NMR techniques. Our work gives a clear microscopic explanation why hole doping of as little as 0.2% may dramatically affect the overall magnetic properties of the entire system. We have found that holes introduced in the LS state of $LaCoO_3$ by substitution of Sr^{2+} for La^{3+} transform the six nearest neighboring Co^{3+} ions to the IS state forming octahedrally shaped spin-state polarons. The formation of spin-state polarons may be a common mechanism present in other Co-based compounds. Spin-state polarons behave like magnetic nanoparticles embedded in an insulating nonmagnetic matrix. Additional charge carriers increase the number of such spin-state polarons, which form a percolative network resulting in a metallic state with long-range FM order at the critical concentration $x_c = 0.18$ [3].

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